Plate-out – more than just a phenomenon? Part 1. Plate-out in the extruder

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Plate-out is an apparently normal problem in PVC processing. Despite this, there are relatively few publications on the subject. There are no satisfactory explanations of the causes, influencing factors and mechanisms. This paper is a summary of the literature on the subject and describes a reliable laboratory method for investigating plate-out and the determination of the influencing factors. The results of the analysis of plate-out are used as the basis for proposed mechanisms of plate-out. The summary provides PVC processors with tips on how to reduce plate-out.

1. INTRODUCTION

Plate-out is an apparently normal problem in PVC processing [2-9]. Bos et al [3] describe plate-out as “the uncontrolled formation of frequently troublesome deposits or coatings on hot or cold metal surfaces in a processing line”. Plate-out first attracted attention in the late 1970s and early 1980s [2, 4, 5].

Parey [2, 4] discusses the influence of the mixing conditions and surface finish of PVC. However, no other authors have paid consideration to these factors. Parey assumed that PVC liquid-stabilised melts tend to be subject to less plate-out than those based on solid stabiliser systems.

Probably the best known and most recognised mechanism for the formation of plate-out in the die was suggested by Lippoldt [5]. This is based on the fact that organic components are only restrictedly soluble in the hot PVC melt and the assumption that less soluble components, such as paraffin waxes, separate out of the melt as a heterogeneous phase and together with tin stabilisers transport inorganic particles to the metal/polymer melt boundary layer. The inorganic particles are deposited here and form the initial point for further depositions while the organic phase migrates further in the direction of extrusion as a “release agent” between the metal and the resin.

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Holtzen and Musiano [6] investigated the influence of the rheology of polymer melts in various dies in order to determine where plate-out forms in the die.

Leskovansky [7] discusses a possible relationship between plate-out formation and oxidised metal surfaces. The work performed by Bussman and Kerr [8] followed a similar direction, but was based on calcium-zinc-stabilised PVC. They ascribe plate-out formation to the oxidation of the steel cylinder and the associated rougher surface towards which superfluous lubricant migrates.

Virtually all authors agree that plate-out mainly comprises inorganic materials such as titanium dioxide, chalk or (lead-based) basic stabilisers. The content of organic compounds such as calcium stearate, lubricants, plasticisers and sometimes even PVC tends to be lower. As
far as plate-out in the die is concerned, it may be assumed that the quantitative composition does not correspond to the composition of the dryblend.

Various people have also observed that titanium oxide or chalk have reduced the incidence of plate-out. This was attributed to the abrasive action of these minerals [3, 8, 9].

The causes, influencing factors and mechanisms have only been partially explained. This paper describes a laboratory method for the investigation of plate-out and demonstrates its reliability. We also present findings, such as different influencing factors on plate-out, and the results of the analysis of plate-out and finally provide some tips as to how PVC processors can reduce plate-out.

2. EXPERIMENTAL

We used the following test formulations:

- dryblend 1: 100 phr S-PVC (k=68), 5 phr chalk, 7 phr polyacrylate-based modifier, 3 phr titanium oxide (rutile) and x phr stabiliser/lubricant Onepack A based on calcium and lead
- dryblend 2: 100 phr S-PVC (k=68), 6 phr chalk, 7.5 phr polyacrylate-based modifier, 4 phr titanium oxide (rutile) and x phr stabiliser/lubricant Onepack B based on calcium and lead
- dryblend 3: 100 phr S-PVC (k=68), 5.5 phr chalk, 6.5 phr polyacrylate-based modifier, 3.5 phr titanium oxide (rutile) and x phr stabiliser/lubricant Onepack C based on calcium and lead.

The components were heated in a hot mixer for 5 minutes to 120°C and then stored for 24 h and then extruded for 90 minutes on a KMDL 25 conical twin-screw extruder.

Extruder settings:

- zone 1 180°C
- zone 2 190°C
- screw temperature control 180°C
- screw speed 20 rpm
- die 195°C
- output rate 3.2-3.5 kg/h
- melt temperature 190-193°C

The extruder screw was filled to approximately 75%. The dryblend was partly gelled in the vent zone. The work was performed without a vacuum. A description of the extrusion die may be found in [10]. The plate-out was evaluated by at least three people for each individual zone. A score of 0 was awarded for no plate-out and 5 for a large amount of plate-out (see the examples in Figure 1). Then, the mean value was calculated for every zone and the total formed from the mean values.

The reliability of the method was tested by mixing dryblend 1 with 5.63 phr of stabiliser/lubricant Onepack A under constant conditions followed by its extrusion (Figure 2). The mean value for the plate-out was 8.03 and the standard deviation 0.6.

3. RESULTS AND DISCUSSION

3.1 Plate-out in the vacuum zone due to sublimation

Recently, a pipe manufacturer found that he was producing approximately 30 m-long pipe sections with fisheyes at regular intervals. The fisheyes were located not only on the internal or external surfaces, but also distributed over the entire cross section. FTIR spectroscopy clearly demonstrated that the main constituent of the fisheyes was definitely pentaerythrite.

The formation of the fisheyes was due to the fact that pentaerythrite is subject to sublimation in the vent zone where the conditions of high melt temperature and vacuum are favourable for sublimation. The additive condensed on the relatively cooler points. As a result of mechanical vibrations or gravity, the sublimate was returned to the extruder where it was mixed with the melt at periodic intervals. The problem was quickly resolved by changing the stabiliser composition [11].
The same thing happens with BHT (ionol) which is added inter alia to pre-stabilise the PVC. Practical experience has also identified the presence of other highly volatile components, such as plasticisers, fatty alcohols and short-chain paraffins, added to the dryblend by the actual manufacturer.

3.2 Plate-out in the die

3.2.1 Influence of the melt temperature

All authors [2, 3, 4, 9] concur that increasing the melt temperature of the polymer melt results in increased plate-out in the die. Parey [2] quotes 175°C as the critical temperature for lead-stabilised systems. He sometimes found extremely severe plate-out in the melt-temperature range of between 175 and 195°C. Bos et al [3] confirm this finding and attribute it to the increased mobility of the additives due to the lower shear stress and melt viscosity. This result was also confirmed with the equipment described in this paper (Figure 3).

On the basis of this finding and our own statistical experiments, it may be assumed that, subject to a certain amount of subjectivity, this method is reliable and relatively precise.

3.2.2 Influence of moisture

It is correctly assumed that moisture encourages the formation of plate-out. To test this, we added defined quantities of distilled water to dryblend 2 with 5.5 phr of stabiliser/lubricant Onepack B in a cold mixer. The plate-out formation is shown in Figure 4. This clearly shows that even relatively low quantities of (additional) moisture in the dryblend, for example 0.05 phr, are responsible for a significant increase in the amount of plate-out. If greater amounts of water are added, the curve flattens out and approaches a limit value.

4. CONCLUSIONS

Extruder operators should, therefore, ensure that the conveying air is dry, that the majority of moisture is extracted in the mixer and that the gelation in the vent zone permits the optimum extraction of the residual moisture. These relatively simple measures permit much longer uninterrupted extrusion times. A further improvement may be achieved by the addition of optimum quantities of anti-plate-out additives.

4.1 Typical compositions of plate-out in the die

Tables 1 and 2 summarise the results of analyses of plate-out in the die. Descriptions of other investigations may be found in [10]. Our investigations confirm qualitatively the data obtained by Lipoid [5]. We found mainly inorganic components (65 to 98%) and fewer organic components, such as lubricants, fatty acids and acrylates. However, it is interesting that, in addition to the ingredients of the formulation, we also identified reaction products from the stabilisation of the PVC. We found up to 15% chloride, which was mainly attributable to calcium and lead in the case of calcium-lead stabilisation and zinc in the case of calcium-zinc stabilisation. Another interesting finding is the fact that the composition of the plate-out in the die is very different from that of the plate-out in the calibrator (we will report on this at a later date). Our analysis of the plate-out in the die reveals that only those components that have migrated from the resin melt are identified, but this does not give any indication of the cause. This indirectly provides a certain confirmation of the general validity of Lippoldt’s mechanism [5].
4.2 Influence of plate-out on gloss

Theoretically, plate-out is a “desired effect” as long as no inorganic particles are entrained and deposited. A thin film of non-polar paraffin or polyethylene waxes prevent the polymer melt from adhering to the hot metal in the extruder and, together with other influencing factors, provide the extrudate with a glossy surface.

If, however, inorganic components of the formulation are also deposited, the PVC surface will be roughened in addition to this wax film. The extrudate will become less glossy. As a practical demonstration of this, we measured the gloss in relation to the extrusion time (Figure 5). The gloss starts to fade noticeably after approximately 45 minutes. After approximately 90 minutes, it is only half its original value. Consequently, gloss measurements represent one possibility for assessing plate-out formation in the die.

4.3 Influence of anti-plate-out additives

Titow [12] and Bos et al. investigated the impact of silicas. Bos et al. [3] described the positive impact of pyrogenic silicas on plate-out formation. The suspected cause was the absorption of incompatible formulation components on the surface of the silica. The possibility of an abrasive action could not be excluded. Also observed was a displacement of the die plate-out in the direction of the calibrator – this was explained by the fact that it is only in this area that incompatible components occur. No impairment of the gloss as a result of the additives was observed.

If this hypothesis is correct, it should be supported by other abrasive additives with a high specific surface. To test this, were investigated highly disperse silica and aluminium oxide.

As Table 3 shows, both silica and aluminium oxide achieve a significant decrease in plate-out. During our investigation, we succeeded in developing a new additive (additive 1 in Table 3) which results in a significant reduction in plate-out in the die. This additive 1 has no impact on the rheology, gloss or weathering properties.

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<tr>
<th>Table 1. Chemical composition (semiquantitative as %) of plate-out in the die during profile extrusion</th>
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<td>Lead</td>
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<td>Calcium</td>
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<th>Table 2. Chemical composition (semiquantitative as %) of plate-out in the die during sheet and pipe extrusion</th>
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Figure 5. Dependence of plate-out in the die on the melt temperature (dryblend 3 with 5.5 phr stabiliser/lubricant Onepack C +0.1 phr water)
5. REFERENCES


(No date given)